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Control of molecular dynamics in intense laser fields

M Mohan*, A Maan and P Jha

Department of Physics and Astrophysics, Delhi University, Delhi-110 007, India

E-mail : sneh@del2.vsnl.net.in

Abstract : In recent years, due to development of ultra-short-pulse laser technology, resulting laser field as high as 10^{16} W/cm^2 can routinely be generated. In such a strong laser field, molecules undergo a variety of nonlinear processes. Many new surprising phenomena have been observed in molecules such as alignment along laser polarization direction, high-harmonic generation, dressed state formation, multiphoton ionization, ultrafast structure deformation, coulomb explosion *etc.* which will be discussed in this article.

Keywords : High-harmonic generation (HHG), multiphoton ionization, coulomb explosion.

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1. Introduction

The study of atoms and molecules in strong laser fields [1–7] with ultra-short-pulse duration has been one of the areas of atomic and molecular physics that has attracted considerable interest recently. The definition of laser-field to be intense, depends upon its application in various situations. In common day life, it is regarded as intense when the laser cuts through a hard material. However, on the microscopic scale, it might be different. It is still possible that the interaction of individual molecules with the same laser is well treated by perturbation theory, and the laser field is therefore, weak. The difference arises from the large difference between our perception of time and the atomic time scale (1 a.u time $\approx 2.4 \times 10^{-17}$ s). Even on atomic scale, different meanings may be used, depending on the situation. In case of interaction of laser with two level systems, the Rabi-frequency describes the strength of the coupling. We say the field is strong, if the Rabi-period is shorter than interaction time (usually the duration of the laser pulse) *i.e.* ($\Omega < \tau_{pulse}$).

In this case, the population is initially pumped to the 'final' level and then back to the initial level *i.e.* absorption is followed by stimulated emission. The result is periodic transfer of population or Rabi oscillations [8]. However, if the final state happens to be continuum, the molecule ionizes or dissociates.

At higher intensities, the Rabi-frequency becomes very large and close to the laser frequency. In such a field, the molecular cloud is distorted and free wavefunction becomes dressed wavefunction while corresponding molecular energy levels are shifted across distances of the same order as the separation between the levels. Under such field, one can optimize laser-molecular interactions with different laser parameters.

For still higher field ($I \geq 10^{14}$ W/cm^2), the laser field becomes appreciably stronger than the inter-field of the molecules resulting stripping off the valence electrons irrespective of the molecular species. At stronger laser fields, new phenomenon occurs in molecules and clusters *e.g.* Coulomb-explosion resulting source of high speed charge particles which can be used for further applications.

As we go to higher intensities of $I \geq 10^{18}$ W/cm^2, we reach to the Super-Intense regime where the interaction with the valence electron is dominant, and the interaction with parent ion is more like a perturbation. At such field, relativistic-correction also become quite important and plays a dominant role.

*Corresponding Author

2. Intense laser systems

To achieve intense laser, one has to squeeze large amount of energy in a sufficiently short pulse time. Various types of table-top intense lasers are available these days. Among them, solid state lasers like Nd : YAG, Nd : YLF lasers and gas lasers like Kr-F eximer, are quite popular. In the high intense regime, the most popular laser is the femtosecond titanium sapphire laser (Ti : Al_2O_3) in combination with chirped pulse amplification (CPA). Tunability in such a system can be achieved with the help of optical parametric amplifier (OPA).

Due to the availability of shorter and shorter pulses, the focussing of lasers to higher intensities have become easier. Example of nano-second pulse laser is that of 10 Hz Nd : YAG laser ($\lambda \simeq 1064$ nm) which produces pulses of approximately $\simeq 10$ ns with energy $\simeq 1$ J corresponding to the pulse power $\simeq 10^8$ W. To achieve the intensity of 10^{14} W/cm^2 from such a laser, this system should be focussed with spherical lense to the area of $A \simeq 10^{-6}$ cm^2. A typical femto-second laser is Kilo-Hertz Ti : sapphire laser with $\simeq 100$ fs pulses with energy $\simeq 1$ mJ. The pulse power $\simeq 10^{10}$ W which is higher than the previous one. From this, the intensity can be achieved to $I \simeq 10^{15}$ W/cm^2 by focussing with a lense of focal length $f \simeq 300$ mm.

In order to understand the behaviour of molecule in a strong field, one has to understand the basic structure of molecule. The simplest molecule is diatomic molecule having two atoms. The binding of two atoms occurs when they are close and new electronic state is formed. The valence electrons from the atoms experience double (or multiple) set of Coulomb interactions which lead them to occupy new electronic states that are of bonding (or anti-bonding) character. For multi-electron molecules *e.g.* NO_2, HOCl, it is the highest occupied molecular orbital (HOMO) state that determines the characteristics of the bond. The orbital may be symmetric or anti-symmetric in character. The electronic state gives rise to potential surface (PES) which in turn, is experienced by the atomic nuclei. In typical diatomic molecule *e.g.* H_2, we have two lowest potential surfaces (bonding and anti-bonding). For polyatomic molecules, the bond is characterized by two quantities : one, by the angle made with the bonds between neighbouring atoms and second, by the bond length. The electronic states above the lowest HOMO state are the excited states. The lowest unoccupied excited state, is called the lowest unoccupied molecular orbital or LUMO.

The positions of HOMO, LUMO and other excited states play an important role in the interaction with the laser field *i.e.* it leads to enhanced excitation if the transition frequency between the states ω_{s_i} is in single or multiphoton resonance with the field. If the excited state (*e.g.* LUMO) to which the molecule is excited due to laser field, has no potential minimum but decreases with internuclear distance r_e, then the molecule will dissociate on the time scales from few femto-seconds to pico-seconds depending upon the nature of potential surfaces and mass of the fragments.

We next consider the vibration motion (or nuclei) in the nuclear-bond about the equilibrium distance r_e in the molecule. The potential surface which has a potential well, looks like potential well of harmonic or anharmonic oscillator (*e.g.* Morse-oscillator). Like harmonic-oscillator, one can quantize the vibration motion of the nuclei about r_e into ground and excited vibrational modes with energy spacing nearly equal to $\simeq \hbar\omega_0$ where ω_0 is the natural frequency of the oscillator. The vibration period T_V varies from 10 fs for a strongly bound system like N_2 to 10's of ps in case of polyatomic molecule. We may have 'strech' modes which modulate the bond length, or 'bend' modes which correspond to the oscillation in the angle of bond about the equilibrium direction with period of bend motion $T_B \sim 100$ fs.

We know that the molecules not only vibrate but can also rotate in space about one or more axes. The speed of rotation depends upon the moment of intertia I about the rotational axis and therefore, rotational constant $B = h/8\,\Pi^2\,cI$ in cm^{-1}. The rotational period of the molecule $T_R \simeq 1/2$ Bc varies from $T_R \simeq 100$ fs to 10's of ps. One has to cool the molecules enough so that the molecules may not be in the thermal distribution of J-states. A short pulse with duration τ_p interacts with the sample on a time-scale very much less than the rotational period (*i.e.* $\tau_p << T_R$) and thus 'freezes' the tumbling of the molecules at one instant so that it might be imagined to be an ensemble of randomly aligned molecules.

In the following sections, we will discuss the various multiphoton processes *i.e.* multiphoton ionization, Coulomb-explosion, high-harmonic generation (HHG), control of alignment or orientation of an ensemble of an aligned molecule *etc.* at an instant of interaction with laser pulse.

3. Multiphoton field ionization and Coulomb-explosion

In the strong field, there may be multiphoton or tunnel

ionization in multi-electron system. Keldysh [9] introduced a useful parameter γ, now known as Keldysh parameter to separate non-linear multiphoton processes, either atomic or molecular, into two regimes, the multiphoton and tunneling regimes. The Keldysh parameter γ, is defined as the ratio of atomic (molecular) electronic energy and field induced energies

$$\gamma = \sqrt{(I_p/2U_p)},$$

where I_p is the ionization potential, $U_p = e^2E^2/4m\omega^2 = I/I_0 4\omega^2$ a.u is the ponderomotive energy and $I = I_0 = 1$ a.u. is the laser intensity, corresponding to 3.5×10^{16} W/cm^2.

In case of H atom, I_p = 13.6 eV = 0.5 a.u, so that for laser intensity with $I = I_0 = 1$ a.u, $\omega = 1$ a.u (with λ = 45.6 nm), $U_p = 1/4\omega^2 = 0.25$ a.u, the Keldysh parameter is

$$\gamma = \sqrt{(0.5/2x0.25)} = 1.$$

Thus for $\gamma < 1$ and for low $\omega < I_p$, where $U_p > I_p$, the ionization rate becomes independent of wavelength and ionization and higher harmonic generation (HHG) can be described by tunneling mechanism.

For $\gamma > 1$, typical of higher frequencies *e.g.* UV, X-ray ionization is by multiphoton process and ionization rate is αI^n.

Tunnel ionization : for $\gamma < 1$, can be understood by considering the distortion of Coulomb–potential of the atom (or molecule) by strong laser field. The height of the potential is raised when the field becomes large and the potential is lowered when the field becomes low. The bound electron thus in the presence of field feels barrier of finite width through which there is a finite probability of quantum tunneling. Ammsov *et al* [10] have given the formula for the quantum tunneling in atom. For strong near infra-red laser field, the tunnel ionization dominates over the multiphoton ionization rate by many order of magnitude.

Multiphoton ionization : in atoms and molecules have been done by several authors [11,12]. A comprehensive study of one, two and four photon ionization of H_2 at the Kr-F laser has been recently studied by Burke group [13]. They have combined R-matrix theory of scattering part with Floquet theory for radiative part as had been employed successfully by Mohan Milfield [14] in laser-induced chemical reactions.

Coulomb-explosion : if the ionization of several electrons in a molecule is rapid due to interaction with laser field, the Coulomb-explosion occurs. The remaining nuclei of the molecule feels massive repulsion force.

The potential energy stored in the system due to Coulomb repulsion between the positively charged nuclei, is rapidly released as kinetic energy shared between the two nuclei that fly apart [15,16]. For a pair of bare nuclei of diatomic molecule like N_2 with $r_e \simeq 10^{-10}$ m, the Coulomb potential energy $\simeq 50$ eV. This energy is equally shared between the two nuclei and the acquired velocity $\simeq 2 \times 10^5$ m s^{-1}. In case of polyatomic molecules and clusters the fragment energy due to Coulomb-explosion may go upto 100 s of keV range [17]. By noting the angular distribution and energy of the fragment, one can find the architecture of the molecule, known as Coulomb-explosion imaging [18].

4. Laser-induced orientation and alignment in molecules

The study of atoms under the impact of intense laser field, leads to various multiphoton processes like ATI (Above Threshold Ionization) and HHG (High-Harmonic Generation). However, if we go little towards complexity *i.e.* in case of molecules and specifically to polar molecules with large permanent dipole moment, which when subjected to intense laser field, shows an interesting phenomenon called as 'Orientation or Alignment Effect'.

The term 'Orientation' has its significance in the fact that most of the chemical reactions are sensitive to the relative orientation of the reactants. So, it is quite desirable to develop a strategy for orienting the molecules in a particular way and controlled manner.

The Orientation of the molecules can be carried out in several ways using static or time-dependent electromagnetic fields, however the HCP (half-cycle pulses) of the form given by $f(t)$ [19]

$$f(t) = \begin{cases} \sum_{j=0}^{N-1} \sin^2[\Pi(t - j\tau)/T] & 0 < t - j\tau < T, \\ 0, & \text{otherwise,} \end{cases}$$

is of particular interest as they form a train of pulses all pointing in the same direction, not flipping the sign of the field for alternative half-cycle and thus, produces better orientation. Here $j = N-1$ and τ is time delay between two sequential HCP's. The rotational period $T_{rot} \simeq h/B$. Now, to explain the term Orientation in a more elaborate and analytical way, let us assume that the electric field takes the form

$$E(t) = E_o f(t)\cos(\omega_o t),$$

where E_0 = electric field amplitude, $f(t)$ = pulse envelope, ω_0 = angular frequency.

Thus, the Hamiltonian will include the terms involving interaction of the dipole moment (μ_0) of the molecule and the electric field E; and also the interaction of polarizability components ($\alpha_\perp$ and $\alpha_{||}$) characteristic of a polar molecule, with the electric field. Thus, the generic Hamiltonian will take the form as given by [20,21]

$$H = BJ^2 + V_\mu(\theta,t) + V_{\text{pol}}(\theta,t),$$

where

B = rotational constant of the molecule,

J^2 = squared angular momentum operator,

θ = angle between electric field and the molecular axis.

The term

$$V_\mu(\theta,t) = -\mu_o E(t)\cos\theta,$$

where

μ_0 = permanent dipole moment of the molecule along the inter nuclear axis and the term

$$V_{pol}(\theta,t) = -\frac{1}{2}[\Delta\alpha\cos^2(\theta,t) + \alpha_\perp]E^2(t),$$

where $\Delta\alpha = \alpha_{\text{II}} - \alpha_\perp$

Thus the resulting TDSE (time-dependent Schrödinger equation) becomes

$$i\hbar\frac{d\psi(\theta,\phi;t)}{dt} = H(t)\psi(\theta,\phi;t).$$

The above TDSE can be solved numerically using either the Split operator technique [22] on a discrete grid or a basis set expansion of the wavefunction in terms of spherical harmonics propagated with a Fourth-Runge-Kutta scheme, with initial state taken as the ground rotational (isotropic) state $J = M = 0$ offering the advantage of rotational excitation only to high J. The measure of orientation can then be obtained as the expectation value of $\cos^n(\theta)$ [20,21]

$$\langle\cos^n(\theta)\rangle(t) = \int_0^{2\pi}\int_0^{\pi}|\psi(\theta,\phi;t)|^2 \cos^n(\theta)\sin(\theta)\,d\theta\,d\phi,$$

In the above equation, n = 1, 2 refers to orientation and alignment parameters or factors, respectively. The orientation parameter and alignment parameter for the case of HF (hydrogen flouride) molecule with time in picosconds (*i.e.* t(ps)) have been plplotted in Figures 1 and 2 . It can be seen that the value of the orientation

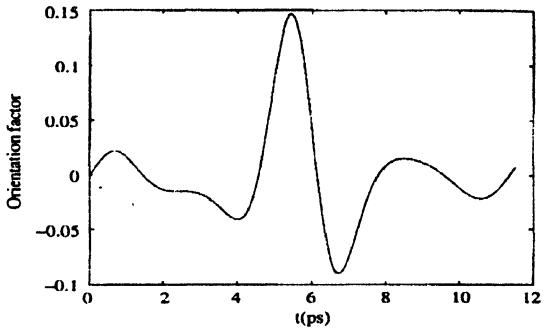

Figure 1. Orientation Dynamics of HF molecule in terms of expectation value of the cosine of angle between the molecular axis and the linearly polarised field polarisation vector *i.e.* <Cos(θ)> *vs.* *t*(ps).

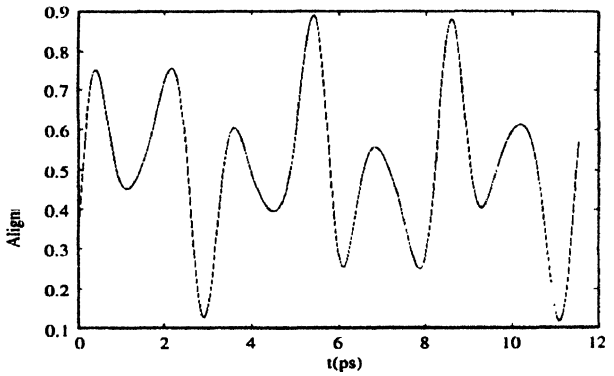

Figure 2. Plot of alignment parameter with time in picoseconds *i.e* <cos²(θ)> *vs.* *t*(ps).

parameter *i.e.* <cos(θ)>(t) varies within the interval [–1,1] and that of alignment parameter varies between 0 and 1. The extermal value of <cos^n(θ)> defines the extent to which the Orientation or alignment is being achieved.

5. HHG (high-harmonic generation) in atoms and molecules

The process of emission of photons started with the Einstein's explaination of the photoelectric effect which is a 'scarce photon' theory. However, with the advent of lasers, it became possible to send thousands or even millions of photons through a typical cross section.Thus, lasers took away the 'scarce photon' theory to 'multiphoton' theory. The high-harmonic is one of the

results of the multiphoton theory. It says that when an quantum system is subjected to an intense laser field, the response of the system to the external field becomes highly nonlinear [23] as the laser intensity rises to the order of 10^{13} W/cm^2 and higher. The result is the radiation of photons by the system at frequencies of multiples of laser fundamental frequency which is normally called as 'harmonic generation (HG)'.

The study of HHG with HRL's (Hyper Raman Lines) is important in the sense that it creates the possibility of obtaining high-frequency light. The process can be explained using an equation as explained below :

Suppose a target A (*i.e.* atom) absorbs q photons (*i.e.* γ); then as a result of the process, we get the same atom and a photon γ' whose energy is q times the energy of the incident photon [24]

$$A + q\gamma(\hbar\omega_L) \rightarrow A + \gamma'(q\hbar\omega_L).$$

To explain the process analytically, we consider the wave function of the form [25] *i.e.*

$$\Psi(t) = c_i(t)|\phi_i\rangle ,$$

where i is the number of states involved in the system and c_i's are the corresponding amplitudes.

The Hamiltonian of the system consists of two types of terms : diagonal and the off-diagonal terms including the energy and the interaction terms, respectively [25].

$$H(t) = \begin{matrix} -\omega_o/2 & \Omega_o\sin(\omega_L t) & \bullet & \bullet & \bullet \\ \Omega_o\sin(\omega_L t) & \omega_o/2 & \bullet & \bullet & \bullet \\ & & \bullet & \bullet & \bullet \\ & & \bullet & \bullet & \bullet \\ & & \bullet & \bullet & \bullet \end{matrix}$$

where ω_L is the laser frequency Ω_0 is the Rabi frequency which is given by

$$\Omega_0 = -\mu.E_0,$$

where μ is the elecric dipole transition matrix element between two states of the system.

Thus, the Schrödinger equation takes the form

$$i\frac{d}{dt}\begin{pmatrix} c_1(t) \\ c_2(t) \\ \bullet \\ \bullet \\ c_i(t) \end{pmatrix} = \begin{pmatrix} -\omega_o/2 & \Omega_o\sin(\omega_L t) & \bullet & \bullet & \bullet \\ \Omega_o\sin(\omega_L t) & \omega_o/2 & \bullet & \bullet & \bullet \\ \bullet & \bullet & \bullet & \bullet & \bullet \\ \bullet & \bullet & \bullet & \bullet & \bullet \\ \bullet & \bullet & \bullet & \bullet & \bullet \end{pmatrix} \begin{pmatrix} c_1(t) \\ c_2(t) \\ \\ \\ c_i(t) \end{pmatrix}$$

and then the time-dependent dipole moment becomes

$$d(t) = \langle\Psi(t)|d|\Psi(t)\rangle,$$

where

$$d = -E(t).r,$$

where

$E(t)$ = Electric Field.

So, Fourier transform of above equation takes the form

$$d(\omega) = \int dt\, e^{i\omega t} d(t)^{|2}$$

The plot of log(d(ω)) with the harmonic order (*i.e* ω/ω_0) gives the required harmonic spectra and thus explains harmonic generation and its charactistics like plateau, cut-off *etc.* Figures 3 and 4 show the harmonic spectra of H_2 molecule and H_2^+ ion, respectively.

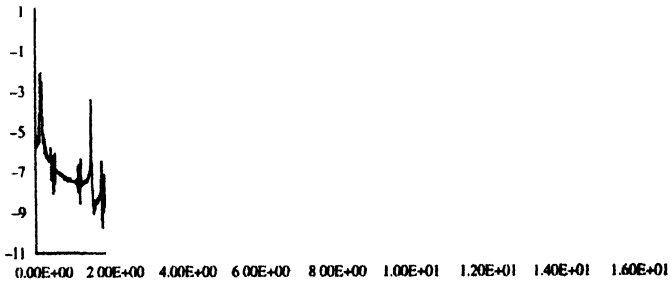

Figure 3. Harmonic spectrum of hydrogen molecule at intensity ~10^{14} W/cm^2 *i.e.* plot of log($d(\omega)$) *vs.* harmonic order.

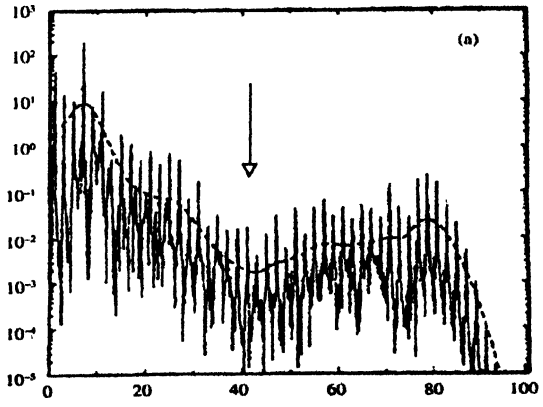

Figure 4. Plot of $d(\omega)$ *vs.* harmonic order for H_2^+ for the intensity ~10^{14} W/cm^2.

With the possibility of aligning the molecules, Velotta *et al* [26] and Corkum *et al* [27] found the modification in HHG in CS_2, H_2 and O_2 molecules. Experimental studies in HHG were done for the first time by Chin's group [28]. Recently, experiments on looking at the symmetry effects (*e.g.* O_2 *versus* N_2) has been done by Lin Group [29] where they have shown that for π_g bonded systems such as O_2, the harmonic cut-off is extended beyond the limit found in the partner atom (Xe), apparently due to suppression of ionizaton leading to an elevated ionization saturation intensity in this molecule.

Ellipticity of laser field is found to play a very sensitive role in the yield of HHG in atoms and molecules [30,31] as even a small value of ellipticity suppresss the re-collision of the electron wavepacket with the core. Thus, ellipticity dependent HHG studies can give directly the information about the electron dynamics. Theoretical work on HHG in H_2^+ and H_2 molecules have been done for the first time by Bandrauk and co-workers [32,33]. Other groups active in this area are of Kopold *et al* [34] and Lein *et al* [35]. Lein *et al* [35] have adopted the numerical technique and have shown that the amplitude and phase of single molecule HHG response in both H_2^+ and H_2, vary as the angle between the molecular axis and the laser polarization direction θ. In their work, dipole amplitude was found which shows a minimum at some intermediate angles θ. (corresponding to where there is a substantial jump in phase of the dipole) and is due to interference in harmonic emission between two atomic centers in the molecule [36].

6. Conclusion

We have discussed several intense-laser-molecular interaction phenomena due to development of laser technology where one can control a light pulse on the time scale of atomic and molecular processes. Another important goal of research in this field is to channel light into a particular chemical bond and catalyze the synthesis of entirely new compounds at room temperature and normal atmospheric pressure. Such type of theoretical and experimental work will help to understand how to create complex vibrations in molecules and eventually to control chemical reactions.

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